Monte Carlo Calculations for the Phase Equilibria of Alkanes, Alcohols, Water, and Their Mixtures

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Abstract

Configurational-bias Monte Carlo simulations were carried out to investigate (i) the self-aggregation of 1-hexanol in n-hexane rich binary solutions, (ii) the partitioning of normal alkane and primary alkanol solutes between water, neat or water-saturated 1-octanol, n-octane, and vapour phases, and (iii) the vapour-liquid phase diagram of the binary mixture of methanol and n-hexane at a temperature of 448 K. The OPLS (optimized potentials for liquid simulations) united-atom force field was used to describe the interactions of the alkanes and alcohols, and the TIP4P (transferable intermolecular potentials 4 point) model was used for water. Analysis of radial distribution functions and their corresponding number integrals supports a micro-heterogenous picture of the 1-hexanol/hexane solutions with the majority of the 1-hexanol molecules being part of hydrogen-bonded clusters with four to six molecules. The OPLS force field yields Gibbs free energies of transfer that are in qualitative, albeit not quantitative agreement with experimental results. Comparison of the partitioning between a helium vapour phase and dry and wet (water-saturated) 1-octanol established that water saturation affects mostly the partitioning of polar solutes, while differences for alkane partitioning were found to be negligible. The vapour pressure of OPLS n-hexane is too low and that of methanol too high, resulting in a binary vapour-liquid phase diagram that deviates significantly from experiment.

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Introduction

Accurate knowledge of phase equilibria and other thermophysical properties of complex mixtures is of enormous importance for the chemical industry. However, given only architecture of the molecules (types of atoms and their connectivity) and the experimental conditions (temperature, pressure, and overall composition), the quantitative prediction of phase equilibria and thermophysical properties remains one of the grand challenges for the field of molecular simulation [1-3]. The success of molecular simulation in advancing our knowledge of complex chemical systems depends on the availability of efficient simulation algorithms and accurate force fields [4-6].

Over the last few years, significant progress has been made in the development of accurate force fields for linear and branched alkanes [7-13]. These alkane force fields were successfully applied for the prediction of multicomponent phase diagrams containing alkanes of rather different molecular weights [14,15] and of the retention order of alkane isomers in gas-liquid chromatography [16]. However, mixtures of nonpolar and polar species pose a greater challenge, and only a few phase equilibrium calculations for these systems have been published [17,18]. Agreement with experiment was found to be much less satisfactory than for alkane mixtures.

The aim of this work is to assess the ability of the popular OPLS (optimized potentials for liquid simulations) force field for organic molecules and of the TIP4P (transferable intermolecular potentials 4 points) water force field to describe the interactions in mixtures containing alkanes, alcohols, and water.

Force Fields

The popular OPLS united-atom and TIP4P force fields developed by Jorgensen and

co-workers [4,5,19,20] was parameterized using isobaric-isothermal Monte Carlo simulations to give accurate liquid densities and heats of vaporization for short alkanes, alcohols, and water at atmospheric pressure. The nonbonded interactions between *pseudo*-atoms, which are separated by more than three bonds or belong to different molecules, are described by pairwise-additive Lennard-Jones (LJ) 12-6 potentials and by Coulombic interactions of partial charges

$$u(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{1}$$

where r_{ij}, ϵ_{ij}, σ_{ij}, q_i and q_j are the separation, LJ well depth, LJ size, and partial charges, respectively, for the pair of atoms i and j. The values of these parameters are listed in Table 1. In contrast to Jorgensen's original description, unlike interactions were computed here using standard Lorentz-Berthelot combining rules [1]. Spherical potential truncations at 14 Å and analytical tail corrections (for the energy, pressure, and chemical potential) were used for the Lennard-Jones interactions [1]. In addition, an Ewald sum with tin-foil boundary conditions ($\kappa \times L = 5$ and $K_{\max} = 5$) was used to treat the long-range electrostatic interactions.

The TIP4P water was represented by a fully rigid structure with an O-H bond of 0.9572 Å and a H-O-H angle of 104.52 deg. Besides one Lennard-Jones site on the oxygen atom with $\epsilon/k_B = 78$ K (where k_B is Boltzmann's constant) and $\sigma = 3.154$ Å, two charge sites on the hydrogen atoms with $q = 0.52$ e, there is one additional charge site with $q = -1.04$ e, which is located on the bisector of the H-O-H angle and shifted away from the oxygen atom towards the hydrogens by 0.15 Å. The alkanes and alcohols were treated as semiflexible molecules. *Pseudo*-atoms were connected by bonds with a fixed lengths of 1.53, 1.43, and 0.945 Å for C-C, C-O, and O-H, respectively, but bond angle bending was governed by harmonic potentials

$$u_{\text{bend}} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \tag{2}$$

with force constants of $k_\theta/k_B = 62500$, 50400, and 55440 K rad^{-2} for C-C-C, C-C-O, and C-O-H bond angles, respectively.[21] The corresponding equilibrium bond angles θ_0 were set to 112, 108, and 108.5. The motion of the dihedral angles ϕ was controlled by the OPLS united-atom torsional potential [19,20]

$$u_{\text{tors}} = c_1[1 + \cos\phi] + c_2[1 - \cos(2\phi)] + c_3[1 + \cos(3\phi)] \tag{3}$$

with $c_1/k_B = 355.03$ K, $c_2/k_B = -68.19$ K, and $c_3/k_B = 791.32$ K for C-C-C-C, $c_1/k_B = 176.62$ K, $c_2/k_B = -53.34$ K, and $c_3/k_B = 769.93$ K for C-C-C-O, and $c_1/k_B = 209.82$ K, $c_2/k_B = -29.17$ K, and $c_3/k_B = 187.93$ K for C-C-O-H.

Simulation Details

A. Binary liquid mixture of 1-hexanol/n-hexane. Configurational-bias Monte Carlo (CBMC) [7,8,22,23] simulations in the isobaric-isothermal ensemble [24] were used to investigate a 3 mole percent mixture of 1-hexanol in n-hexane at a temperature of 298.15 K and a pressure of 101.5 kPa. In addition to the usual translational, rotational, CBMC conformational, and volume moves, a CBMC swatch move was used [25]. In this latter move the CH_2OH subunit of a randomly selected alcohol molecules is swapped with a methyl group of a randomly selected alkane molecule (i.e., switching the identity of the two molecules involved), thereby allowing very efficient sampling of the spatial distribution of alcohol molecules. The simulation was carried out for 30 1-hexanol and 970 n-hexane molecules starting from an initial configuration in which the alcohol molecules were randomly dispersed. 30000 and 50000 Monte Carlo cycles (one Monte Carlo cycle consists of N moves where N is the total number of molecules in the system) were employed for the equilibration and production periods, respectively.

B. Solute partitioning between water, 1-octanol, 1-octane, and vapour phases. Simulations in the isobaric version of the Gibbs ensemble[26,27] (at $T = 298$ K and $p = 101.3$ kPa) were carried out for four different two-phase systems (see Table 2): G/OL, helium/(dry) 1-octanol; G/OL*, helium/(water-saturated) 1-octanol; G/W, helium/water; and G/O, methane/n-octane. Because of the low vapour pressures of 1-octanol, n-octane, and water, the concentrations of these molecules in the vapour phases would be very low. Therefore swap moves for these molecules were not considered. For each of the four systems, five independent simulations of either 10^5 or 2×10^5 Monte Carlo cycles (production period) were carried out.

C. Vapour-liquid phase equilibria of n-hexane/methanol. Configurational-bias Monte Carlo simulations in the grand-canonical ensemble using histogram-reweighting techniques [17,28,29] were employed to determine the n-hexane/methanol phase diagram at $T = 448.15$ K. This temperature is sufficiently below the critical temperature of each component; finite-size effects are small and simulations of a relatively small system still yields accurate results. In this case, a simulation cell of box length $L = 22$ Å was used. The liquid phase contained approximately 100 methanol (methanol rich) and 40 n-hexane (n-hexane rich) molecules. The ratio of Monte Carlo moves was 70 % insertion/deletion, 15 % translation and 15 % rotation. Simulations for the liquid phase were 10 million Monte Carlo steps (MCS), while 5 million MCS were used for simulations of the vapor phase. Over the course of the simulations, the number of molecules of each component and the energy were saved to a list updated every 250 MCS. Upon completion of the simulations, these lists were combined self-consistently [30] and the necessary probability distributions were extracted.

Results and Discussion

A. Binary liquid mixture of 1-hexanol/n-hexane. Visual inspection of a "movie" of the simulation showed a micro-heterogenous system with a large extent of non-random mixing with hydrogen-bonded 1-hexanol aggregates. The ensemble averaged fraction of 1-hexanol molecules found in aggregates of a given size was calculated (see Figure 1), and it is clearly evident that the 1-hexanol molecules prefer to self-assemble in cluster with 4 or 5 molecules. These large aggregates were found to predominantly consist of cyclic structures, similar to those found in water cluster in the gas phase. Compared to linear structures, the cyclic arrangements with at least four members allow for one additional hydrogen bond and have relatively little ring strain. Approximately one in six 1-hexanol molecules is found as free monomeric species. It is also interesting to note that the fraction of 1-hexanol molecules in dimers is very low. These observations are in qualitative agreement with experimental measurements on the same system by Gupta and Brinkley [31], who observed that about two thirds of the 1-hexanol were hydrogen-bonded. Using a theory with hydrogen-bond cooperativity, Gupta and Brinkley predicted that 11% and 56% of the 1-hexanol molecules are part of dimers and larger clusters, respectively. The radial distribution functions (RDFs) of 1-hexanol oxygen-oxygen and methyl-methyl pairs are shown in Figure 2. The strong preference to form hydrogen-bonded clusters is reflected in the unusually large first and second peaks in the oxygen-oxygen RDF. Cluster formation is also evident in the methyl-methyl RDF, particularly the broad second peak is caused by the larger clusters, where the alkyl tails point away from the hydrogen-bonded core region.

B. Solute partitioning between water, 1-octanol, 1-octane, and vapour phases. The calculated Gibbs free energies of transfer, ΔG, and the corresponding experimental values [32-34] are summarized in Table 3. It was found that the calculated

$\Delta G_{\text{G}\to\text{OL}}$ were mostly lower (except for methane, propane, and methanol) than their experimental counterparts (with a mean unsigned deviation for all eight solutes of about 1.3 kJ/mol), whereas both the $\Delta G_{\text{G}\to\text{W}}$ and $\Delta G_{\text{G}\to\text{O}}$ were higher than the experimental values (both with a mean deviation of 1.4 kJ/mol). It is important to note that the OPLS/TIP4P force fields correctly reproduce the minimum in $\Delta G_{\text{G}\to\text{W}}$ for ethane among the n-alkanes. In addition, the approximately 10 kJ/mol difference for alcohols between $\Delta G_{\text{G}\to\text{OL}}$ and $\Delta G_{\text{G}\to\text{O}}$, and a larger difference of about 30 kJ/mol in G$\to$W between an alkane and the alcohol with the same number of carbon units (e.g., methane and methanol) are all qualitatively reproduced by the OPLS force field. The effect of dissolved water on solubilities in the water-saturated 1-octanol phase was studied in an additional set of simulations (the G/OL* case), which required a fixed composition (determined from a short pre-simulation for the W/O system) and the solvent molecules were thus confined to remain in the liquid phase. Comparing $\Delta G_{\text{G}\to\text{OL*}}$ to $\Delta G_{\text{G}\to\text{OL}}$, it can be seen that the dissolved water increases the solubility for polar solutes (e.g., methanol) and slightly decreases the solubility of non-polar solutes.[35] These results compare favorably with the experimental data of Dallas and Carr [32] who reported $\Delta G^*_{\text{OL}\to\text{OL}}$ from -0.97 to -0.76 kJ/mol for methanol to 1-butanol, and a value of 0.25 kJ/mol for n-nonane.

C. Vapour-liquid phase equilibria of n-hexane/methanol. Monte Carlo simulations were used to determine the vapour-liquid phase behavior of the binary mixture n-hexane(1)/methanol(2) predicted by the OPLS united-atom models. A comparison of the predicted phase diagram and the experimental data of Zawisza [36] is shown in Figure 3. The OPLS united-atom model for n-hexane significantly over-predicts the critical temperature. As a result, the vapor pressure for pure n-hexane at 448.15 K is significantly below the experimental value. On the other hand, the OPLS methanol model under-predicts the critical temperature, resulting in a vapor pressure that is

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significantly above the experimental value at 448.15 K. These shortcomings in the description of the pure components result in mixture phase diagram that deviates significantly from experiment. Of particular interest is the location of the azeotrope. Experimentally an azeotrope is found at $x_{hexane} = 0.2878$, $P = 30.7$ bar, however the OPLS model predicts an azeotrope at $x_{hexane} = 0.054$, $P = 34.58$ bar.

Conclusions

Configurational-bias Monte Carlo calculations in various ensembles were carried out to investigate the properties of alkanes, alcohol, and water mixtures. It is found that the OPLS/TIP4P force fields[4,5] are able to capture the qualitative features of all systems studied here. In particular, micro-heterogenous structures were observed for 1-hexanol/n-hexane and water/1-octanol mixtures supporting structural pictures that were inferred from indirect experimental observations. However, the OPLS/TIP4P are not able to yield predictions that are in quantitative agreement with experiment, with the largest disagreement observed for the methanol/n-hexane phase diagram.

List of symbols

$K_{\max}$ Upper bound of the reciprocal space vector in Ewald- summation.

G   Gas phase, helium or methane.

O   n-octane phase.

OL   1-octanol phase.

OL*   Water-saturated 1-octanol phase.

W   Water phase.

L Box length.

N	Total number of molecules in the system.
c_1, c_2, c_3	Torsional potential parameters.
k_B	Boltzmann's constant.
k_θ	Bending force constant.
q_i	Partial charge on the atom i.
r_{ij}	Separation of the atoms i and j.
$u(r_{i,j})$	Intermolecular interaction energy for the pair of atoms i and j.
u_{bend}	Harmonic bending potential.
u_{tors}	Torsional potential.
ϵ_{ij}	Lennard-Jones well depth for the atoms i and j.
ϵ_0	Vacuum permittivity.
κ	Ewald screening parameter.
ϕ	Dihedral angle.
σ_{ij}	Lennard-Jones size for the atoms i and j.
θ	Bond angle.
θ_0	Equilibrium bond angle.

Acknowledgements

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Tables

Table 1. Intermolecular Force Field Parameters for the OPLS United-Atom Force
Fields.

(Pseudo-)atom	σ [Å]	ϵ/k_B [K]	q [e]
CH_4	3.730	147.9	
$CH_3(-CH_3)$	3.775	104.1	
$CH_3(-CH_2R)$	3.905	88.1	
$(R-)CH_2(-R)$	3.905	59.4	
$CH_3(-OH)$	3.775	104.1	+0.265
$CH_3(-CH_2-OH)$	3.775	104.1	
$(R-)CH_2(-OH)$	3.905	59.4	+0.265
$(R-)O(-H)$	3.070	85.6	−0.700
$(RO-)H$			+0.435

Table 2. Simulation Details for the Solute Partitioning Calculations.

	OPLS			
	G→OL	G→OL*	G→W	G→O
No. MC cycles	10^6	10^6	5×10^5	5×10^5
N(He)	600	600	600	0
N(CH$_4$)	20	20	20	580
N(C$_2$H$_6$)	20	20	20	50
N(C$_3$H$_8$)	1	1	1	10
N(C$_4$H$_{10}$)	1	1	1	2
N(CH$_3$OH)	1	1	1	1
N(C$_2$H$_5$OH)	1	1	1	1
N(C$_3$H$_7$OH)	1	1	1	1
N(C$_4$H$_9$OH)	1	1	1	1
N(H$_2$O)	0	24	864	0
N(1-octanol)	240	240	0	0
N(n-octane)	0	0	0	240

Table 3. Gibbs Free Energies of Transfer.

solute	simulation				experiment [32-34]			
	G→OL	G→OL*	G→W	G→O	G→OL	G→OL*	G→W	G→O
CH_4	2.68_4	2.81_8	9.4_2	1.09_2	2.14		8.37	
C_2H_6	-2.74_7	-2.56_9	8.2_4	-4.27_2	-2.68		7.66	
C_3H_8	-4.64_{15}	-4.50_{13}	9.7_5	-6.52_2	-5.27		8.20	
C_4H_{10}	-8.7_3	-8.8_3	10.7_7	-10.72_4	-7.780		8.70	
CH_3OH	-15.80_6	-17.3_3	-19.3_2	-3.28_{16}	-16.17	-17.14	-20.19	-5.40
C_2H_5OH	-20.2_5	-21.1_3	-19.5_4	-7.43_{11}	-18.22	-19.15	-20.95	-9.00
C_3H_7OH	-22.8_5	-23.4_5	-18.8_4	-10.57_{10}	-20.98	-21.81	-20.36	-11.55
C_4H_9OH	-27.6_7	-27.6_5	-18.3_5	-14.54_8	-23.88	-24.64	-19.86	-15.44

The subscripts give the statistical uncertainties in the last digit(s).

Figure Captions

Figure 1. Fraction of 1-hexanol molecules found in clusters as function of aggregation number.

Figure 2. Site-site radial distribution functions for the 1-hexanol/n-hexane mixture. Top: Oxygen-oxygen pairs; bottom: methyl-methyl pairs (both belonging to 1-hexanol molecules).

Figure 3. Pressure-composition diagram for the binary mixture of n-hexane (1) and methanol (2). Circles and solid lines depict the experimental data [36] and calculated compositions, respectively.